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(54) Title: ELECTROLUMINESCENCE IN LIGHT EMITTING POLYMERS FEATURING DEAGGREGATED POLYMERS**(57) Abstract**

In general terms, the present invention includes a light emitting polymeric material, the light emitting polymeric material capable of producing electroluminescence upon being provided with a flow of electrons, the light emitting polymeric material comprising a plurality of polymeric chains comprising polymeric chains each having substituent moieties of sufficient number and size and extending from the polymeric chain and about a substantial portion of the circumference about the polymer chain so as to maintain the polymeric chains in a sufficiently deaggregated state (referred to herein as a "strapped" polymer), so as to substantially prevent the redshifting of the electroluminescence and the lowering of light emission efficiency of the electroluminescence.

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ELECTROLUMINESCENCE IN LIGHT EMITTING POLYMERS FEATURING DEAGGREGATED POLYMERS

This application claims the benefit of U.S. Provisional Application Serial No. 60/023,071 filed August 2, 1996.

Technical Field

The present invention is in the field of light-emitting polymers and light emitting devices
5 produced therefrom.

Background

Conjugated polymer based light-emitting devices have become an extensive area of academic and industrial research since the report of electroluminescence (EL) in poly(phenylene vinylene) (PPV) in 1990 [1].

10 A great number of different conjugated polymers have been found to exhibit EL including PPVs [1-3], poly(phenylphenylene vinylene) [4], polyphenylenes [5-7], polythiophenes [8-9], polyquinolines [10], polypyridines [11-12], poly(pyridyl vinylenes) [12-14] and many copolymers of these materials.

In addition to many different materials, numerous configurations have been used to change and
15 improve device performance. For instance, the use of additional layers to improve device efficiency

has been known for some time [2,15]. Inserting a hole-transport (electron blocking) layer between the anode and emitting polymer or an electron-transport (hole-blocking) layer between the cathode and emitting polymer can greatly improve efficiency by confining the majority carrier to the emitting layer. A well known hole-transport (electron blocking) layer is poly(vinyl carbazole)

5 (PVK) which has a large band gap (3.5 eV) and is itself luminescent [16-18].

Despite these advances there remains a need for improvements in the electroluminescence performance of light emitting polymers. Particularly, there remains a need to improve the performance of exiplex-forming bilayer devices so as to reduce or eliminate the redshifting believed to be associated with the aggregation of polymeric chains within the emitting polymer.

10 It is a goal of the present invention to produce light emitting polymer and light emitting polymer devices made which give light emissions having reduced redshifting.

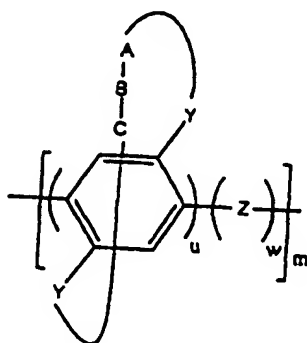
In view of the present disclosure or through practice of the present invention, other advantages may become apparent.

Summary of the Invention

15 In general terms, the present invention includes a light emitting polymeric material the light emitting polymeric material capable of producing electroluminescence upon being provided with a flow of electrons, the light emitting polymeric material comprising a plurality of polymeric chains comprising polymeric chains each having substituent moieties of sufficient number and size and extending from the polymeric chain and about a substantial portion of the circumference about the

20 polymer chain so as to maintain the polymeric chains in a sufficiently deaggregated state (referred to herein as a "strapped" polymer), so as to substantially prevent the redshifting of the electroluminescence and the lowering of light emission efficiency of the electroluminescence.

It is preferred that the polymer of the present invention comprises polymeric chains selected from the group consisting of alternating and random copolymers, having comprising the structure:



wherein m is the degree of polymerization;

Y is selected from the group consisting of $-CH_2$, O , S , CO and NR_2 wherein R is an alkyl group containing 1 to 16 carbon atoms;

A is selected from the group consisting of $(CH_2)_n$, $(CH_2CH_2O)_n$, $(CH_2CH_2O)_nNR$ wherein R is an alkyl group containing 1 to 16 carbon atoms, and aryl groups having 6 to 14 carbon atoms;

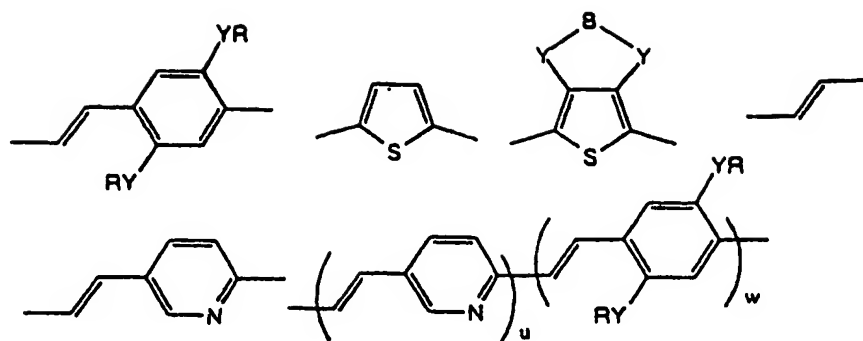
B is selected from the group consisting of $(CH_2)_n$, aryl groups having 6 to 14 carbon atoms, and calixarene having 18 to 200 carbon atoms;

wherein u may be of a value independently selected from the group 1 to 6, inclusive;

wherein w may be of a value independently selected from the group 1 to 6, inclusive;

wherein n may be of a value independently selected from the group 0 to 6, inclusive; and

wherein Z may be a structure selected from the group consisting of:



wherein R is an alkyl group containing 1 to 16 carbon atoms,

wherein Y is selected from the group consisting of -CH₂, O, S, CO and NR₂ wherein R is an alkyl

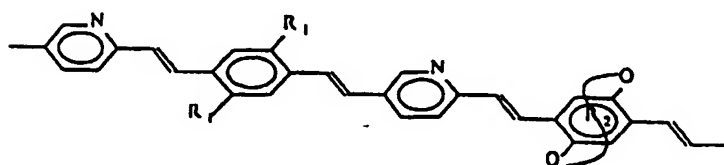
10 . group containing 1 to 16 carbon atoms;

B is selected from the group consisting of $(CH_2)_n$, aryl groups having 6 to 14 carbon atoms, and calixarene having 18 to 200 carbon atoms;

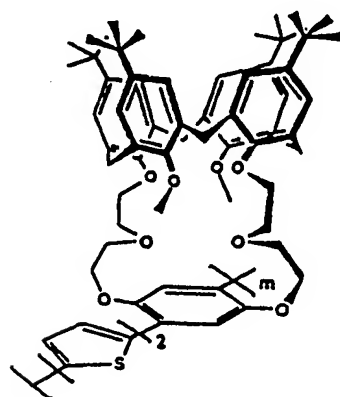
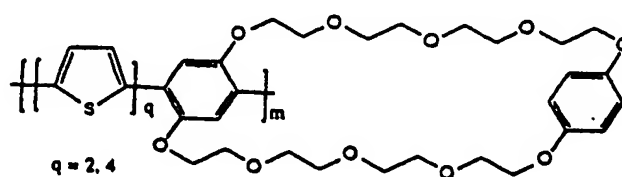
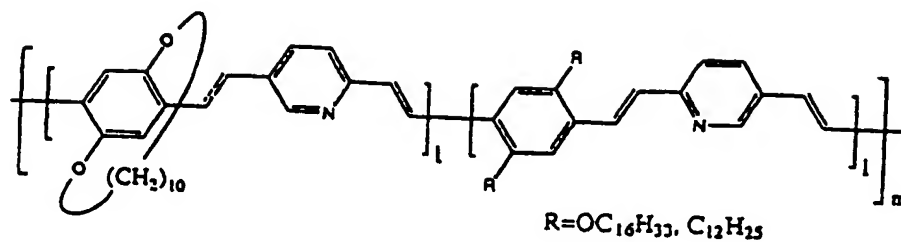
wherein u may be of a value independently selected from the group 1 to 6, inclusive; and

wherein w may be of a value independently selected from the group 1 to 6, inclusive.

15 The electron transporting polymer may include polymeric chains selected from copolymers having the structure:



Some specific examples of polymers used in the present invention include:



The light emitting polymeric material may also be used in single layer, bilayer or other multiple layer devices, using the polymeric material of the present invention. In the case of a single polymeric layer device, the polymeric material of the present invention may be used as the electron transporting/electron blocking layer. In the case of a bilayer or multi-layer devices, the polymeric material of the present invention may be used as the electron transporting layer in conjunction with an electron blocking layer of another appropriate polymer, such as might be selected from the group consisting of poly(vinylcarbazole).

The present invention also includes a light emitting device comprising a light emitting polymeric material according to the present invention in all of its embodiments, and a source of electrical current so as to supply the light emitting device with a flow of electrons capable of producing electroluminescence from the device.

Other examples of synthetic methods are described in reference 27 below.

These devices may be constructed in accordance with deposition and assembly techniques known in the art. The present invention may be used in the creation of a wide variety of lighting and lighted displays, giving the many advantages associated with polymeric materials.

In accordance with the present invention, results are presented for bilayer devices using PVK as a hole-transport layer and a family of copolymers of PPV and poly(pyridyl vinylene) PPyV with various side groups as the emitting layers. The absorption, photoluminescence and electroluminescence spectra indicate that the PL and EL are attributed to the formation of an exciplex at the PVK/copolymer interface for all the copolymer systems studied. An exciplex, like an excimer, is an excited state complex, except that an exciplex is formed between two different molecules (polymers in this case) rather than identical ones for an excimer [19]. Contrary to

expectations, earlier reported devices do not exhibit exciplex formation. For example, Greenham *et al* reported a bilayer device with CN-PPV and PPV, but the EL matches the PL and EL of a single CN-PPV film [3]. Results for other bilayer configurations also do not support exciplex formation [2]. Osaheni and Jenekhe [20] have observed exciplex formation in bilayers of PBO and TTA, but only for PL, although they do suggest that exciplexes may be important processes in organic light-emitting devices [20-21]. PL and EL due to exciplex formation has been reported in *blends* of PVK and a multiblock copolymer by Karasz and coworkers [17], but devices with separate layers were not investigated.

Brief Description of the Drawings

10 Figure 1 depicts three chemical structures relevant to the present invention: (a) a copolymer of PPyV and PPV with side groups $R=C_{12}H_{25}$ or $COOC_{12}H_{25}$, (b) a copolymer with side group $R_1=OC_{16}H_{33}$ and strap $R_2=C_{10}H_{20}$, and (c) a hole-transport layer poly(vinyl carbazole).

Figure 2 depicts plots showing absorbance of a single layer of PVK, a single layer of copolymer, and a bilayer of PVK/copolymer: (a) PPyVP($COOC_{12}H_{25}$)₂V, (b) PPyVP($C_{12}H_{25}$)₂V and (c) 15 "strapped" copolymer.

Figure 3 shows photoluminescence of (a) PPyVP($C_{12}H_{25}$)₂V film (dashed line), PVK/PPyVP($C_{12}H_{25}$)₂V bilayer film (solid line), PVK film (O) (b) PPyVP($COOC_{12}H_{25}$)₂V film (dashed line), PVK/ PPyVP($COOC_{12}H_{25}$)₂V bilayer film (solid line), PVK film (O), and (c) strapped copolymer film (dashed line), PVK/strapped copolymer bilayer film (solid line), PVK film 20 (O).

Figure 4 shows electroluminescence (solid lines) for a (a) ITO/PVK/ PPyVP(COOC₁₂H₂₅)₂V/Al device and a (b) ITO/PVK/strapped copolymer/Al device, and photoluminescence (dashed lines) for bilayer films of PVK and (a) PPyVP(COOC₁₂H₂₅)₂V and (b) strapped copolymer.

Figure 5 shows current density-voltage characteristics (O) and brightness-voltage characteristics of an ITO/PVK/PPyVP(COOC₁₂H₂₅)₂V/Al device. Inset shows a comparison between a single layer, ITO/ PPyVP(COOC₁₂H₂₅)₂V/Al, device (□) and the bilayer device (O). The bilayer device is 10 times brighter at 10 times lower current density implying a 100 times improvement in efficiency.

Detailed Description of the Preferred Embodiment

In accordance with the foregoing summary of the invention, the following presents a detailed description of the preferred embodiment of the invention which is presently considered to be its best mode.

The synthesis of the PPyVPV copolymers is described elsewhere [22]. Figure 1(a) shows the molecular structure of poly(pyridyl vinylene phenylene vinylene) (PPyVPV). We report results for copolymers with side groups R=COOC₁₂H₂₅ and C₁₂H₂₅. Figure 1(b) shows the same copolymer with a "strap" across the phenyl ring in alternate PPV segments. For the second copolymer the side groups are R₁=OC₁₆H₃₃ with a strap R₂=C₁₀H₂₂. The copolymers are soluble in common organic solvents such as tetrahydrofuran (THF), xylene, and chloroform. The PVK (Fig. 1(c)) was purchased from Aldrich Chemical Co.

The PL and EL measurements were made using a PTI QM1 luminescence spectrometer. The absorption measurements were made using a Perkin Elmer Lambda 19 UV/Vis/NIR spectrometer. The current-voltage characteristics were measured using two Keithley 195A multimeters. The voltage was applied using a HP 6218A dc power supply. Quantum efficiency measurements were

made using a calibrated QTH lamp and a United Detector Technologies Silicon Photodiode (UV-100).

The samples for PL and absorption measurements were spin cast on quartz. PVK was spin cast (~3000 rpms) from a 10 mg/ml solution in THF. The copolymers were all spin cast (~1000 rpms) from xylene (~ 10 mg/ml) so the underlying PVK layer was not dissolved. For devices the polymers were spin cast on indium tin-oxide (ITO) substrates, which had previously been cleaned. The PVK layer in the bilayer configurations was dried for ~ 30 seconds in a laminar flow hood before the copolymer layer was spin cast. All fabrication steps for the devices were conducted in an ambient atmosphere in a Class 100 cleanroom. Aluminum electrodes were thermally evaporated onto the copolymer surface at low pressures ($< 10^{-6}$ torr). The active area of the devices was 7 mm².

Results and Discussion

Figure 2 shows the absorbance for single and bilayer systems. Each of the plots shows the absorbance of a single layer of PVK, a single layer of a copolymer, and a bilayer configuration of PVK and the corresponding copolymer. The onset of PVK absorption is at 3.5 eV and shows two spectral features at 3.6 and 3.75 eV similar to previous reports [6,7]. In each of the three cases (a), (b) and (c) of Fig. 2 the absorbance of the bilayer configuration is the sum of the absorbance of each of the individual layers. No new ground to excited state transitions are present. Photoluminescence excitation (PLE) results (not shown) for each of the systems confirm these results.

The photoluminescence for the single layer and bilayer configurations are shown in Fig. 3. The PL (excited at 3.6 eV) of a PVK film is shown in Fig. 3a, 3b and 3c by the open circles (O) and peaks at 3.05 eV similar to previous reports [6,7]. The dashed line is the PL of a single layer film of

each copolymer, (a) PPyVP(C₁₂H₂₅)₂V, (b) PPyVP(COOC₁₂H₂₅)₂V and (c) the strapped copolymer. The spectra are similar with each of the peaks at ~ 2.1 eV with the exception of the strapped copolymer which also has a significant shoulder at 2.25 eV. The PL of the copolymer films, which peak near 2.6 eV [23], are significantly redshifted from that of the solution PL (not shown). The PL redshift from solution to film is due to aggregation in the copolymer films [23].

The solid lines in Fig. 3 are the PL spectra for the bilayer configurations of PVK and each of the copolymers. In each case the bilayer films were excited at 3.6 eV an energy that is greater than the band gap of PVK. In each case, more prominently in Figs. 3b and 3c, there is PL emission at the same energy as the PVK PL emission (3.1 eV). However, the main feature in the PL of the bilayer films is located at 2.5 eV for (a) PPyVP(C₁₂H₂₅)₂V and (b) PPyVP(COOC₁₂H₂₅)₂V and at 2.4 eV for the (c) strapped copolymer. Emission at these energies is not observed for individual films of either PVK or the copolymers indicating that the emission is due to a completely different species, the exciplex. When the excitation energy is lowered below 3.4 eV (band gap of PVK) the emission due to the exciplex is drastically reduced. In addition, varying the concentration or thickness of the copolymer or PVK films in the bilayer configuration will change the relative strengths of the exciplex peak and PVK peak.

PPyVP(C₁₂H₂₅)₂V and PPyVP(COOC₁₂H₂₅)₂V have nearly identical PL results, which is expected since the side chains tend to perform the same function in both copolymers. The single layer PL results for the strapped copolymer in Fig. 3c show a completely new feature, a high energy shoulder. The high energy shoulder is closer to the solution PL and is attributed to unaggregated sites in the film. The C₁₀H₂₀ strap around every other phenyl ring tends to disturb the aggregation that occurs in the other copolymers of this family. The same shoulder (now on the low energy side)

also appears in the bilayer film, indicating the PL has contributions from exciplex sites and from unaggregated regions of the strapped copolymer.

The bilayer devices have turn-on voltages ~ 12-16 volts with current densities between 0.1 and 0.5 mA/mm². The devices can easily be seen in a brightly lit room and have internal quantum efficiencies ~ 0.1-0.5%. Figure 5 shows the current-voltage (O) and voltage-brightness (solid line) characteristics for a typical ITO/PVK/PPyVP(COOC₁₂H₂₅)₂V/Al bilayer device. The inset of Fig. 5 shows a comparison between a single layer device (ITO/PPyVP(COOC₁₂H₂₅)₂V/Al) and the bilayer device shown in the main plot. The bilayer device is ten times brighter at an order of magnitude lower current density which means the bilayer device is ~ 100 times more efficient than the single layer device.

In the devices the electrons are injected from the Al electrode into the conduction band of the copolymer, but they are confined at the PVK/copolymer interface due to a large barrier. The holes injected from the ITO also may be confined at the interface by a somewhat smaller barrier. The increased number of electrons and holes in the interface region increase the probability of recombination via exciplex emission. In addition the buried interface severely reduces the non-radiative recombination that otherwise will occur near the electrodes.

Conclusion

In summary, the present invention demonstrates the presence of exciplex emission in heterojunctions of PVK and PPyVP(R)₂V. The addition of a C₁₀H₂₀ strap on every other phenyl ring in the copolymer reduces the aggregation in the films. Emission from the strapped copolymer bilayers is a combination of light from exciplex and unaggregated sites. The exciplex is the primary method of electroluminescence in the bilayer devices. The bilayer devices we have fabricated show

a 100 times increase in efficiency compared to single layer devices due to charge confinement and exciplex emission at the interface.

The following references are hereby incorporated herein by reference:

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The contents of U.S. Provisional Patent Application Serial Number 60/023,071 are hereby incorporated herein by reference.

In view of the present disclosure or through practice of the present invention, it will be within the ability of one of ordinary skill to make modifications to the present invention, such as through the use of equivalent arrangements and compositions, in order to practice the invention without departing from the spirit of the invention as reflected in the appended claims.

Poly(pyridyl Vinylene Phenylene Vinylene)s: Synthesis and Solid State Organizations

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Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

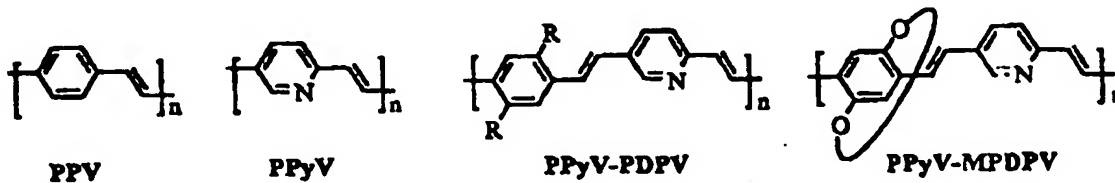
Abstract: Poly(pyridyl vinylene phenylene vinylene)s were synthesized by Heck coupling procedures. These materials display large red shifts in their optical absorption which protonation or alkylation of the pyridyl nitrogen. Some of the polymers were found to be liquid crystalline. The protonated or alkylated versions exhibit highly organized structures due to charge-transfer interactions between polymer chains.

Fu:1

INTRODUCTION

Conjugated polymers have attracted much attention due to their electrical conductivity,¹ interesting optical,² nonlinear optical,³ and more recently electroluminescent properties.⁴ Since their discovery in 1990, polymer-based light-emitting diodes (PLED) have been investigated intensively for potential applications in flat panel displays. PLED generally have the following advantages: 1) long term stability, 2) ease of fabrication, 3) wide spectral range. Poly(phenylene vinylene)s (PPV) are among the most studied PLED polymers and are most often prepared by elimination reactions on precursor polymers. Particularly interesting PPV derivatives are those with electron-poor cyano-substituted vinyl groups. These materials showed higher efficiencies in bilayer structures.⁵ Inspired in part by this later work, we recently reported the synthesis of all of the regioisomers of poly(methyl pyridinium vinylene (PMPyV), a very electron poor isoelectronic analog of PPV.⁶ It has been demonstrated that PMPyV, its parent polymer poly(pyridyl vinylene) (PPyV), and other analogs are promising materials for the construction of LED devices.^{4,7} In those devices, environmentally stable metals such as Al, Cu and Ag were used as electron injection electrodes. As a continuation of our investigations of new PPV analogs, we report herein the synthesis and properties of copolymers comprised of alternating units of poly(pyridyl-2,5-vinylene)s and poly(2,5-disubstituted phenylene vinylene) which we abbreviate as PPyV-PDPV. In this paper we describe the synthesis of these copolymers under Heck coupling conditions.¹⁰

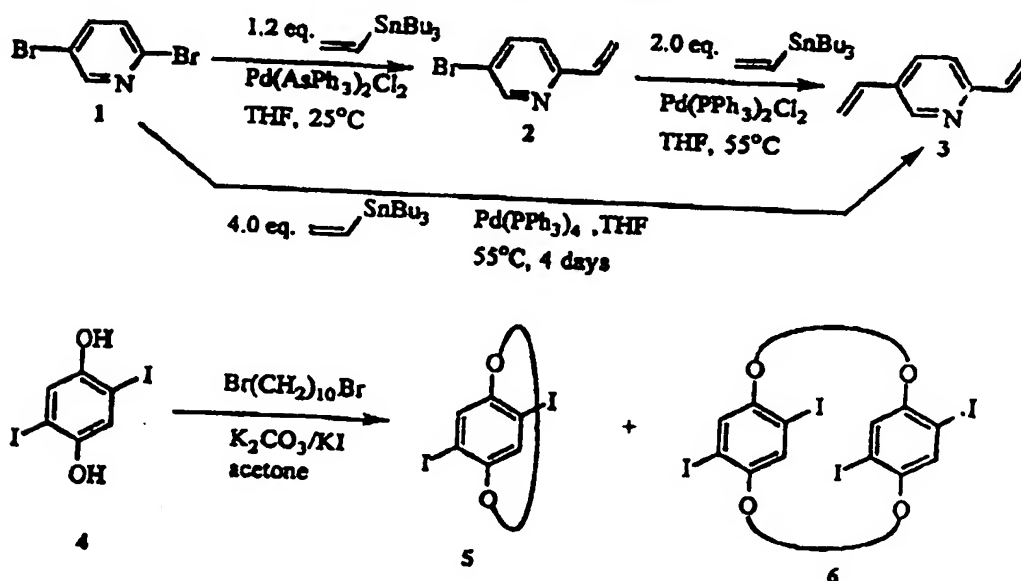
Our interest in PPyV-PDPVs was further stimulated by their structural similarities to known liquid crystalline rigid polyesters.⁸ The preparation of such self-organizing structures is of interest for the study of the factors which control the conducting and electroluminescent properties of these materials. We also anticipated that some of the PPyV-PDPVs may exhibit novel electronic and self-assembling properties associated with their alternating strongly electron-rich and electron-poor structures. Recent photophysical studies⁹ have shown that the photoluminescent properties of conjugated polymers are highly dependent on their solid state organizations. In most cases conjugated polymers show greatly reduced photoluminescent (PL) quantum efficiencies in solid state relative to those obtained in dilute solution. This reduced efficiency is believed due to the strong interchain interactions which provide rapid nonradiative decay mechanisms. To reduce interchain interactions we have prepared the macrocycle containing copolymers PPyV-MPDPV.



RESULTS AND DISCUSSION

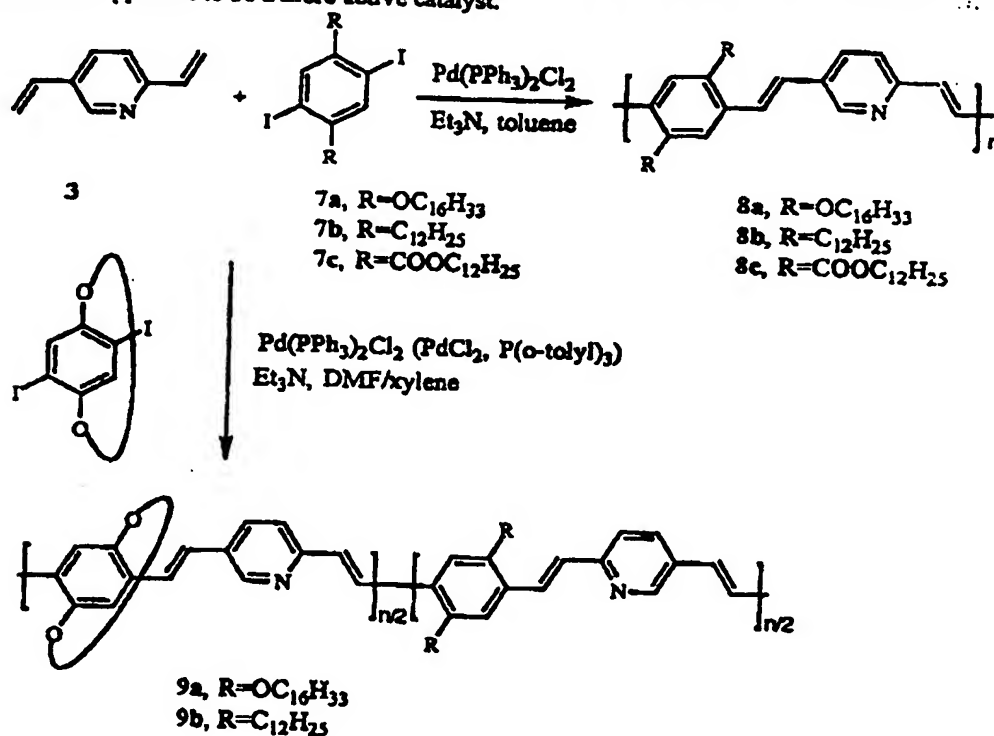
Synthesis

The syntheses of 2,5-divinylpyridine and the macrocyclic monomers are described in Scheme 1. We previously found that by using $\text{Pd}(\text{AsPh}_3)_2\text{Cl}_2$ as a catalyst 2,5-dibromopyridine (1) reacted with vinyltributyltin selectively at the more reactive 2-position to give 5-bromo-2-vinylpyridine (2) in 85% yield.²⁶ Further reaction with 2 at the 5-position using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ occurs at an elevated temperature to produce 2,5-divinylpyridine (3) in 50% yield. This two-step procedure was replaced by an one-step reaction catalyzed by $\text{Pd}(\text{PPh}_3)_4$ in the later part of our studies. While the reaction requires prolonged heating (55°C , 4 days) and an excess of vinyltributyltin (4 eq.), it offers a simplified purification procedure and an improved yield of 80% (a 43% overall yield was obtained for the two step procedure). Purification of 3 requires first a distillation under reduced pressure, to give a mixture of vinyltributyltin, 3, and a trace amount of 2. Further purification of the resulting mixture by flash column chromatography gave 3 as clear liquid in high purity (>99.5% by NMR). Monomer 3 was polymerized with the diiodide monomers under Heck reaction conditions immediately after purification in order to avoid free radical polymerization of the vinyl group. Dilute CH_2Cl_2 solutions of 3 could be stored for a period of one month in the dark at 0°C and were chromatographed before use. The 1,4-(oxydecanyloxy)-2,5-diiodobenzene macrocyclic monomer (5) was easily prepared by a Williamson ether synthesis. In this case, a 1:1 mixture of 2,5-diiodo-1,4-dihydroquinone (4) and the commercially available 1,10-dibromodecane were slowly added to a suspension of K_2CO_3 and KI in acetone via a syringe pump over a period of three days. The high dilution conditions were designed to maximize the formation of 5, however, a substantial amount (15%) of the undesired adduct, 6, was also produced. Since 5 and 6 were similar in physical properties, their separation was only possible through tedious gravity column chromatography ($\text{CH}_2\text{Cl}_2/\text{hexane}$ (5:95), SiO_2). Compound 5, was the first fraction and isolated in 25% yield. The structures of 5 and 6 were confirmed by ^1H and ^{13}C NMR in conjunction with mass spectrometry.



Scheme 1

As shown in Scheme 2, we have employed Heck coupling reactions for the copolymer syntheses.¹⁰ For the purpose of fine-tuning the band structures of the non-macrocycle containing polymers, we synthesized polymers containing disubstituted phenylene units with different electron donating (or withdrawing) abilities. Monomers 7a, 7b and 7c were readily synthesized via standard organic transformations. The polymerizations to form polymers 8a, 8b, and 8c were conducted in toluene at 110°C using Pd(PPh₃)₂Cl₂ as a catalyst. In all cases, the precipitation of Et₃N⁺T⁻ was observed during the polymerization. The precipitation of polymers 8b and 8c was also apparent after 24 hours. To circumvent these problems and improve the efficiency of the coupling reactions, we used modified conditions for the preparation of polymer 9a and 9b. These conditions included a mixed solvent system consisting of DMF and xylene (1:1), for improved solubility, and Pd(P(o-tolyl))₂Cl₂ which appeared to be a more active catalyst.



Scheme 2

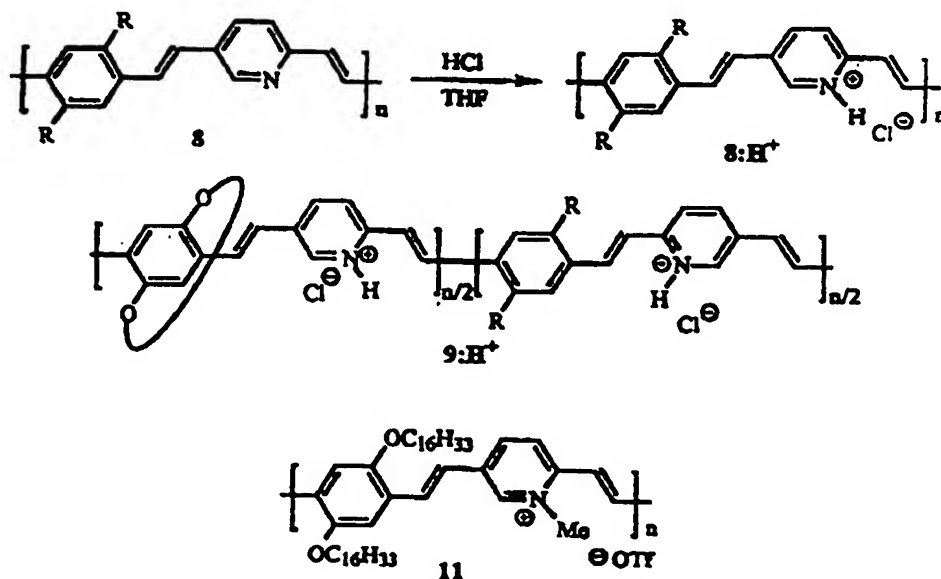
The polymerization results are listed in Table 1. The polydispersity indexes were 1.8-2.0 as expected for a step-growth polymerization. Among polymers of a series 8, we find that 8a displays a higher molecular weight which is consistent with the more reactive nature of dialkoxy substituents and the higher solubility of polymer in the reaction solvent. The lower yields and molecular weights for polymer 8b and 8c are likely due to the increased steric hindrance of the R groups and decreased polymer solubility. The mixed solvents provided a minor improvement for the synthesis of polymer 9a. However by using the mixed solvent with the alternative catalyst, Pd(P(o-tolyl))₂Cl₂ we observed a six fold increase in 9b's molecular weight over the related polymer 8b. Purification of the polymers involved precipitation from acetone and Soxhlet extraction with methanol. Polymers 8a, 9b, 9c are highly soluble in various organic solvents such as CH₂Cl₂, THF, and toluene whereas polymers 8b and 8c are less soluble. All of the polymers are highly colored and fluoresce strongly in solution.

Table 1: Results of Polymerization

Polymer	Isolated yield	Mn	Color
8a	95%	21,000	dark red
8b	88%	5,600	yellow
8c	90%	9,500	orange
9a	97%	22,000	bright orange
9b	98%	40,000	bright yellow

Properties

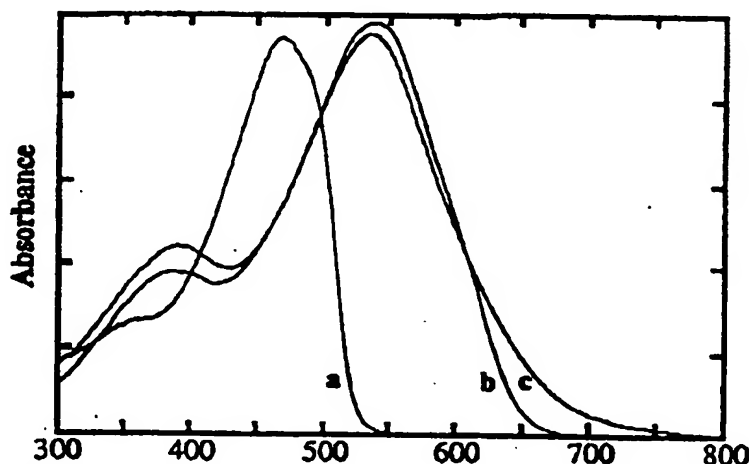
The pyridine units of the copolymers are readily protonated with aqueous HCl. This transformation is accompanied by a dramatic color change (e.g. red to dark purple for polymer 8a) which is due to the donor-acceptor nature of the polymer's electronic structure. Hence it appears that optical transitions involve a charge transfer from the donating dialkoxy phenyl moieties to the pyridine residue which is stabilized by protonation. Treatment of polymer 9a with an excess of methyl triflate in CH_2Cl_2 gives polymer 11 which also displayed similar color changes. Table 2 lists the absorption maxima for all the neutral and cationic polymers. All of the cationic polymers display strong red shifts relative to their neutral forms. Consistent with our characterization of these transitions as having a charge transfer nature, the magnitude of the shifts are consistent with the electron donating (or withdrawing) abilities of the side chains. Consequently, the largest shifts are observed for the dialkoxy groups (8a and 9a) and the diester (8b) displayed the smallest effects. The UV-Vis spectra of polymers 8a after protonation and methylation (11) are shown in Figure 1. The neutral polymer (8a) displays a λ_{max} at 466 nm which is totally absent in the protonated and methylated forms which have respective λ_{max} values of 537 nm and 532 nm.



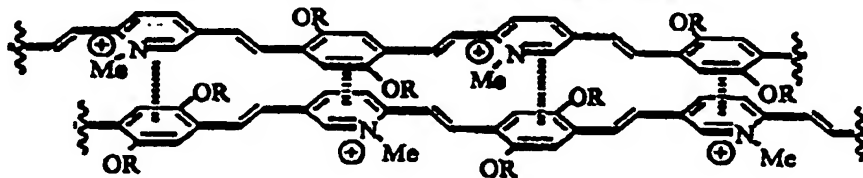
Scheme 3

Tab. 2: UV-vis Data for Neutral and Protonated Polymers

Polymer	λ_{max} (nm)	λ_{H^+} (nm)	$\Delta\lambda$ (nm)
8a	466	537	71
8b	408	450	42
8c	426	452	26
9a	465	532	67
9b	443	502	59

Figure 1. UV-Vis spectra of polymer 8a (a), the protonated form ($8a:H^+$) (b), and polymer 11 (c).

DSC analysis of the polymers showed no detectable phase transitions up to 350°C. However, variable temperature x-ray diffraction studies (Figure 2) indicate that polymers 8a and 11 display liquid crystalline phases at elevated temperatures. The mesophases are of the lamellar Sanidic (Σ) variety¹² in which the polymer chains exhibit a "board-like" biaxial organization in the layers. Based upon the lack of wide angle peaks, we conclude that 8a has very weak interpolymer correlations. We therefore label polymer 8a's mesophase as a disordered Sanidic (Σ_d). Methylation of 8a produces a greatly enhanced (100) diffraction and creates a new reflection at 3.47 Å which indicates a stronger interaction between the polymer chains. We believe that this additional order originates from interpolymer charge-transfer interactions (Scheme 4). Due to the additional wide angle peak at 3.47 Å in polymer 11, we assign this material as an ordered sanidic phase (Σ_o). This two dimensional organization is novel since it creates a precise registry between polymer chains. Other PPV derivatives generally only have nematic order between the polymer chains. The incorporation of macrocycles in the monomers diminishes co-facial chain-chain interactions. XRD studies of polymers 9a and 9b show only weak diffraction characteristics of a very low degree of organization.



Scheme 4

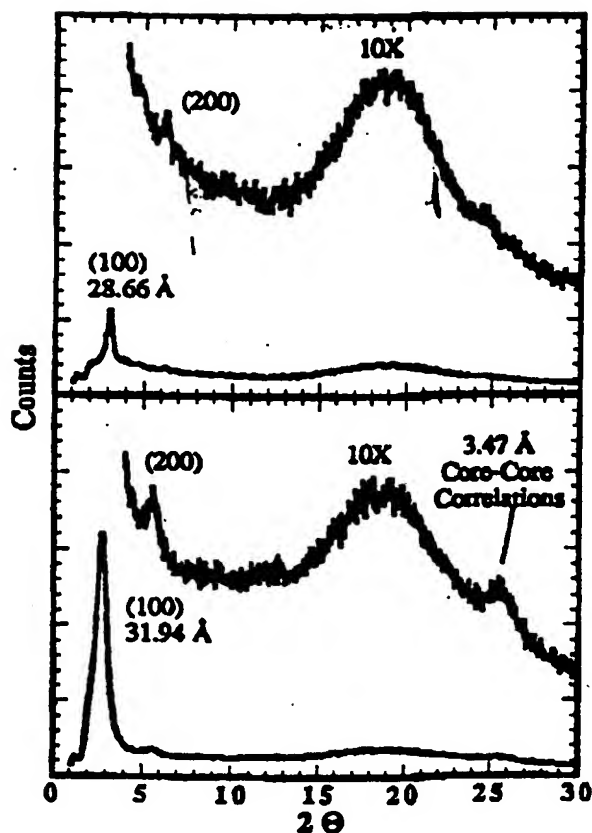


Figure 2. X-ray diffraction at 200°C of polymer 8a (top) and polymer 11 (TfO⁻ salt) (bottom).

CONCLUSION

Polymers 8a, 8b, and 8c have been shown to be promising materials for the fabrication of LED devices. However, the electroluminescent quantum efficiencies of these materials are still low. As mentioned earlier, this is in part the result of the interchain interactions. However, the high degree of charge transfer interaction between polymer chains in 11's Σ_c phase is novel and should result in other interesting electronic properties. The macrocycle containing polymers 9a and 9b, were designed to overcome the problem of interchain quenching. Indeed, the initial photoluminescent studies on these polymers show improved efficiencies and the detailed photophysical studies are currently under way.

EXPERIMENTAL

All experiments were carried out under argon atmosphere. THF was distilled from sodium/benzophenone. DMF were dried over alumina and degassed before use. Vinyltributyltin,¹³ and 4,¹⁴ 7a¹⁴ and 7b¹⁵ were prepared according to literature procedures. Monomer 7c¹⁴ was easily prepared for a previously reported intermediate. 2,5-dibromopyridine (Aldrich), Pd(PPh₃)₄ (Strem), P(o-tolyl)₃ (Aldrich) and PdCl₂ were used as received. NMR spectra were recorded with a Bruker AC-250 (250 MHz) spectrometer. UV-vis spectra were obtained using Hewlett Packard 8453 spectrometer. GPC was performed on a Rainin HPXL solvent delivery system with a RI-1 refractive index detector and a Shodex GPC KI-80M column. Molecular weights are reported relative to polystyrene standards.

2,5-Divinyl Pyridine (3): A THF (100 mL) solution of tetrakis(triphenylphosphane) palladium (100 mg, 8.65x10⁻⁴ mmol), 2,5-dibromopyridine (3.50 g, 14.8 mmol) and vinyltributyltin (18.0 g, 56.8 mmol) was heated at reflux for 5 days. After removal of THF by rotary evaporator, the resulting residue was subjected to distillation under reduced pressure to remove a mixture of 5-bromo-2-vinyl pyridine and vinyltributyltin. The resulting material was further purified by flash column chromatography (SiO₂, EtOAc/hexane, 1:10) to give 3 as a clear liquid (1.55 g, 80%). ¹H NMR (CDCl₃) δ 8.43 (s, 1H), 7.52 (s, 1H), 7.12 (d, 1H), 6.64-6.72 (m, 2H), 6.05 (d, 1H), 5.64 (d, 1H), 5.32 (d, 1H), 5.18 (d, 1H); ¹³C δ 154.6, 147.7, 136.3, 132.9, 132.6, 131.5, 120.6, 117.7, 115.4; MS 132 (M+1).

1,4-(Oxydecanoxy)-2,5-Diiodobenzene (5): A mixture of 2,5-diiodo-1,4-dihydroquinone (7.24 g, 20.0 mmol), 1,10-dibromodecane (6.00 g, 20.0 mmol) and acetone (30 mL) was added to a 500 mL RB flask containing potassium carbonate (30.0 g, 21.7 mmol), potassium iodide (0.50 g, 3.0 mmol) and acetone (300 mL) via a syringe pump over a period of three days while maintaining the reaction at reflux. After another three days, the acetone was removed with a rotary evaporator. The solid residue was then neutralized with dilute HCl, and extracted with CH₂Cl₂ (3 x 100 mL). Removal of CH₂Cl₂ followed by flash column chromatography (SiO₂, CH₂Cl₂ (hexane, 5:95) gave the desired product as a white solid (2.0 g, 20%). ¹H NMR (CDCl₃) δ 7.27 (s, 1H), 4.16-4.34 (m, 4H), 1.56-1.66 (b, 4H), 1.06-1.24 (m, 6H), 0.90-0.94 (b, 2H), 0.70 (b, 4H); ¹³C δ 152.6, 126.9, 89.1, 70.6, 27.6, 27.4, 23.7; MS 518 (M⁺NH₄).

Polymer 8a: A mixture of divinylpyridine (0.493 g, 3.76 mmol), 1,4-dihexadecanoxy-2,5-diiodobenzene (3.05 g, 3.76 mmol), triethylamine (2.0 mL), bis(triphenylphosphene) palladium dichloride (30 mg, 0.043 mmol) and toluene (10 mL) was heated at 110°C for 24 hours. The reaction was then diluted with 20 mL of toluene and poured into 600 mL of acetone to give a red precipitate. The resulting precipitate was collected by suction filtration. Further purification by Soxhlet extraction with methanol for 24 hours afforded polymer 8a as dark red solid (2.45 g, 95%). ¹H NMR (CDCl₃) δ 8.67, 7.82, 7.49, 7.46, 7.17, 7.12, 4.04, 1.88, 1.52, 1.23, 0.84; ¹³C δ 155.1, 151.4, 151.0, 148.7, 132.7, 131.8, 128.8, 127.6, 126.8, 125.2, 124.8, 111.2, 110.4, 69.4, 69.3, 31.9, 29.7, 29.5, 29.4, 29.2, 26.2, 22.7, 14.1; Anal. Calcd: C, 82.28; H, 11.02; N, 2.04. Found: C, 79.09; H, 10.67; N, 1.88.

Polymer 8b: Monomers 3 and 7b were reacted under the same conditions as 8a to give polymer 8b in 88% yield. ¹H NMR (CDCl₃) δ 8.76, 7.89-7.98, 7.45-7.55, 7.08-7.21, 2.65-2.80, 1.57-1.62, 1.26, 0.88.

Polymer 8c: Monomers 3 and 7c were reacted under the same condition for the synthesis of polymer 8a to give polymer 8c in 90% yield. ¹H NMR (CDCl₃) δ 8.76, 8.36, 8.29, 7.91-8.08, 7.52, 7.08-7.13, 4.41, 1.84, 1.25, 0.86.

Polymer 9a: A mixture of 3 (581.4 mg, 4.43 mmol), 5 (1.108 g, 2.215 mmol), 7a (1.797 g, 2.215 mmol), triethylamine (3.0 mL), bis(triphenylphosphene)palladium dichloride (30 mg, 0.043 mmol), xylene (7.0 mL) and DMF (7.0 mL) was heated at 135°C. After 24 hours the reaction mixture was diluted with 10 mL of xylene and poured into a flask containing 600 mL of acetone. The resulting orange solid was collected by suction filtration and washed with methanol. Removal of the residue methanol gave polymer 9a as bright orange solid in 97% yield. ¹H NMR (CDCl₃) δ 8.69, 7.82-7.87, 7.49-7.56, 7.25, 7.11-7.16, 4.47, 4.24, 4.04, 1.87, 1.53, 1.23, 1.00, 0.84, 0.82, 0.73.

Polymer 9b: A mixture of 3 (121.6 mg, 0.927 mmol), 5 (231.8 mg, 0.46 mmol), 7b (307.5 mg, 0.463 mmol), triethylamine (0.5 mL), palladium dichloride (5.4 mg, 0.0304 mmol), tri(o-tolyl)phosphine (18.6 mg, 0.0304 mmol), xylene (1.5 mL) and DMF (1.5 mL) was heated at 135°C. After 3 hours, the formation of yellow precipitate was observed. The reaction mixture was then diluted with 3 mL of xylene and poured into a flask containing 500 mL of acetone. The resulting yellow solid was collected by suction filtration and washed with methanol. Removal of the residue methanol gave polymer 9b as bright yellow solid in 98% yield. ¹H NMR (CDCl₃) δ 8.73, 7.84-7.90, 7.41-7.51, 7.26, 7.05-7.14, 4.48, 4.26, 2.80, 1.77, 1.62, 1.24, 0.82-0.85, 0.74.

ACKNOWLEDGMENTS

Funding from the Office of Naval Research is greatly appreciated.

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16. Monomer 7c was readily synthesized from the diacid chloride derivative reported in ref. 14.

In The Claims:

1. A light emitting polymeric material said light emitting polymeric material capable of producing electroluminescence upon being provided with a flow of electrons, said light emitting polymeric material comprising:

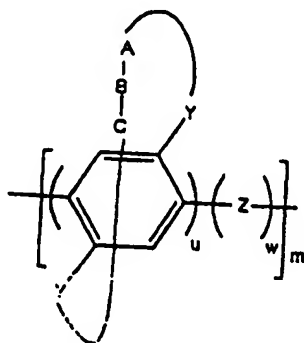
5

a plurality of polymeric chains comprising polymeric chains each having substituent moieties of sufficient number and size and extending from said polymeric chain and about a substantial portion of the circumference about said polymer chain so as to maintain said polymeric chains in a sufficiently deaggregated state, so as to substantially prevent the redshifting of said

10 electroluminescence and the lowering of light emission efficiency of said electroluminescence.

2. A light emitting polymeric material according to claim 1 comprising polymeric chains selected from the group consisting of alternating and random copolymers, having the structure:

15



20

wherein m is the degree of polymerization;

Y is selected from the group consisting of $-CH_2$, O , S , CO and NR_2 wherein R is an alkyl group containing 1 to 16 carbon atoms;

5 A is selected from the group consisting of $(CH_2)_n$, $(CH_2CH_2O)_n$, $(CH_2CH_2O)_nNR$; wherein R is an alkyl group containing 1 to 16 carbon atoms, and aryl groups having 6 to 14 carbon atoms;

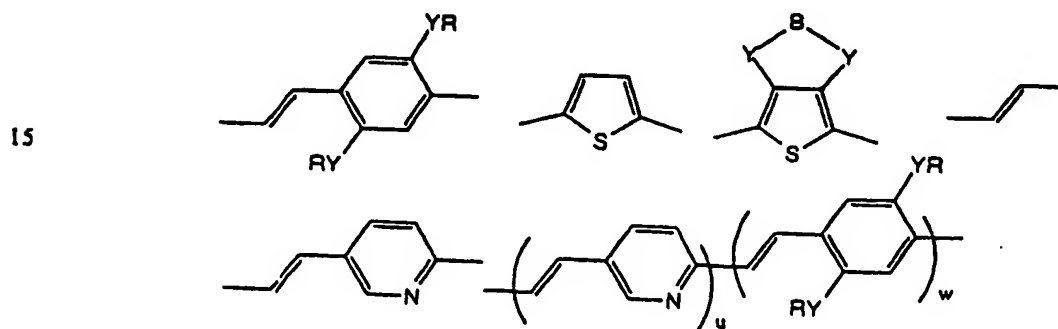
B is selected from the group consisting of $(CH_2)_n$, aryl groups having 6 to 14 carbon atoms, and calixarene having 18 to 200 carbon atoms;

wherein u may be of a value independently selected from the group 1 to 6, inclusive;

10 wherein w may be of a value independently selected from the group 1 to 6, inclusive;

wherein n may be of a value independently selected from the group 0 to 6, inclusive; and

wherein Z may be a structure selected from the group consisting of :



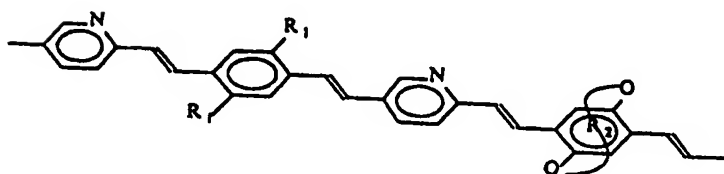
wherein R is an alkyl group containing 1 to 16 carbon atoms;

20 wherein Y is selected from the group consisting of $-CH_2$, O , S , CO and NR_2 wherein R is an alkyl group containing 1 to 16 carbon atoms;

B is selected from the group consisting of $(CH_2)_n$, aryl groups having 6 to 14 carbon atoms, and calixarene having 18 to 200 carbon atoms;

wherein u may be of a value independently selected from the group 1 to 6, inclusive; and
wherein w may be of a value independently selected from the group 1 to 6, inclusive.

- 5 3. A light emitting polymeric material according to claim 1 wherein said polymer comprises polymeric chains selected from the group consisting of copolymers, having the structure:



10

wherein R_1 is $OC_{16}H_{33}$ and R_2 is $C_{10}H_{20}$.

4. A light emitting polymeric material according to claim 1 wherein said polymeric material is further provided with a layer of an electron blocking polymer.

15

5. A light emitting polymeric material according to claim 4 wherein said electron blocking polymer is selected from the group consisting of poly(vinylcarbazole).

6. A light emitting polymeric material said light emitting polymeric material capable of producing electroluminescence upon being provided with a flow of electrons, said light emitting polymeric material comprising:

5 a plurality of polymeric chains comprising polymeric chains each being provided with rotaxenes of sufficient number and size and extending from said polymeric chain and about a substantial portion of the circumference about said polymer chain so as to maintain said polymeric chains in a sufficiently deaggregated state, so as to substantially prevent the redshifting of said
10 electroluminescence and the lowering of light emission efficiency of said electroluminescence.

7. A light emitting polymeric material according to claim 6 wherein said polymeric material is further provided with a layer of an electron blocking polymer.

15 8. A light emitting polymeric material according to claim 7 wherein said electron blocking polymer is selected from the group consisting of poly(vinylcarbazole).

9. A light emitting device, said device comprising a light emitting polymeric material according to claim 1, and a source of electrical current so as to supply said electron transporting polymer with a
20 flow of electrons.

10. A light emitting device, said device comprising a light emitting polymeric material according to claim 2, and a source of electrical current so as to supply said electron transporting polymer with a flow of electrons.

5 11. A light emitting device, said device comprising a light emitting polymeric material according to claim 3, and a source of electrical current so as to supply said electron transporting polymer with a flow of electrons.

12. A light emitting device, said device comprising a light emitting polymeric material according to claim 4, and a source of electrical current so as to supply said electron transporting polymer with a flow of electrons.

13. A light emitting device, said device comprising a light emitting polymeric material according to claim 5, and a source of electrical current so as to supply said electron transporting polymer with a flow of electrons.

14. A light emitting device, said device comprising a light emitting polymeric material according to claim 6, and a source of electrical current so as to supply said electron transporting polymer with a flow of electrons.

15. A light emitting device, said device comprising a light emitting polymeric material according to claim 7, and a source of electrical current so as to supply said electron transporting polymer with a flow of electrons.

5 16. A light emitting device, said device comprising a light emitting polymeric material according to claim 8, and a source of electrical current so as to supply said electron transporting polymer with a flow of electrons.

10 17. A light emitting device, said device comprising a light emitting polymeric material according to claim 1, and a source of electrical current so as to supply said electron transporting polymer with a flow of electrons, said device selected from the group consisting of single layer, bilayer and multi-layer light emitting devices.

15 18. A light emitting device, said device comprising a light emitting polymeric material according to claim 6, and a source of electrical current so as to supply said electron transporting polymer with a flow of electrons, said device selected from the group consisting of single layer, bilayer and multi-layer light emitting devices.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/13417

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 26/06, 26/12, 28/06; H01L 33/00

US CL : 526/256, 258; 257/10, 40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/256, 258; 257/10, 40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, P	US 5,597,890 A (JENEKHE) 28 January 1997, columns 4-40.	1-18
A	US 5,254,633 A (HAN et al.) 19 October 1993.	1-18
A	US 4,356,429 A (TANG) 26 October 1982.	1-18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

22 SEPTEMBER 1997

Date of mailing of the international search report

06 OCT 1997

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